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Evaluation of the Orion Divalent Specific Ion Electrode

Interagency Energy/Environment R&D Program Report

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The Orion Divalent Cation Specific Ion Electrode #93-32 was evaluated for suitability in monitoring or in-situ marine applications as a magnesium ion sensor. The electrode was tested with three separate modules for the following parameters: accuracy, precision, temperature dependence, short - and long-term stability, durability, sensitivity to variations in light intensity and flow conditions, response time as a function of temperature and concentration, and variability between modules. The sensor, a "liquid ion-exchange" type, was evaluated at 10°C and 25°C in freshwater, synthetic seawater (35-, 20- and 5-ppt salinity) and natural waters (IAPSO Standard Seawater, Atlantic Ocean Water and Chesapeake Bay Water). A description of sensor, theory of operation and a summary of the test results are included. Although two of the detectors supplied with the electrode failed prematurely, the third replacement module performed well in all media with an accuracy of 5% in magnesium concentration when properly calibrated on a daily basis. The response times were generally longer than expected, ranging on the average from 3 minutes in seawater to 26 minutes in untreated freshwater. The electrode was relatively insensitve (±0.2 mV) to external wire motion, flow conditions or variations in light intensity.

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by

Gary K. Ward
National Ocean Survey
National Oceanic and Atmospheric Administration
Rockville, Maryland 20852

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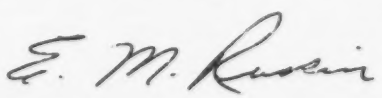
FOREWORD

The Test and Evaluation Laboratory of the National Ocean Survey's Office of Marine Technology, National Oceanic and Atmospheric Administration, conducts work to:

- test and evaluate new or state-of-the art sensors for use in the marine environment
- determine the error bounds on chemical sensors' performance to obtain data quality assurance information
- determine suitability of new sensors for in situ or field use
- evaluate new methods for the chemical analysis of seawater
- develop standards and calibration equipment and procedures to maintain a quality assurance program for measurements in the marine environment.

New chemical sensors are under continual test and evaluation to assure that the most accurate results possible are obtained. If specific ion electrodes are to be used to measure chemical parameters in seawater, they must be evaluated directly in the medium of interest, i.e., seawater. This report investigates the basic characteristics of specific ion electrodes in a variety of water types to determine their suitability for in situ or monitoring applications.



Eugene M. Russin
Chief, Sensor Test Branch
Test and Evaluation Laboratory

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The Orion Divalent Cation Specific Ion Electrode #93-32 was evaluated for suitability in monitoring or in situ marine applications as a magnesium ion sensor. The electrode was tested with three separate modules for the following parameters: accuracy, precision, temperature dependence, short- and long-term stability, durability, sensitivity to variations in light intensity and flow conditions, response time as a function of temperature and concentration, and variability between modules. The "liquid ion-exchange" sensor was evaluated at 10°C and 25°C in freshwater, synthetic seawater (35-, 20- and 5-ppt salinity), and natural waters (IAPSO Standard Seawater, Atlantic Ocean water and Chesapeake Bay water). A description of the sensor, theory of operation, and a summary of the tests and results are included. Although two of the modules supplied with the electrode failed prematurely, the third replacement module performed well in all media with an accuracy of 5% in magnesium concentration when properly calibrated on a daily basis. The response times were generally longer than expected, ranging on the average from 3 minutes in seawater to 26 minutes in untreated freshwater. The electrode was relatively insensitive ($\pm$0.2 mV) to external wire motion, flow conditions, or variations in light intensity.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ACS -- American Chemical Society
cm -- centimeter
h -- hour
IAPSO -- International Association for the Physical Sciences of the Oceans
ISA -- ionic strength adjustor
log -- logarithm
min -- minute
ml -- milliliter
mo -- month
mV -- millivolt
ppt -- parts per thousand
RSE -- residual standard error

SYMBOLS

A -- activity
Ag -- silver
AgCl -- silver chloride
Ca^{2+} -- calcium
Cl -- chloride
°C -- degrees Celsius
E -- electrode potential
E° -- electrode constant
F -- Faraday's constant
I -- ionic strength
°K -- degrees Kelvin
KCl -- potassium chloride
M -- molarity
m -- total ion concentration
Mg^{2+} -- magnesium ion
$MgCl_2$ -- magnesium chloride
R -- universal gas constant
S -- electrode slope
T -- time, temperature
T_1 -- response time within 1 mV
T_{95} -- 95% response time
z -- ionic change
γ -- activity coefficient
Δ -- delta

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SECTION 1

INTRODUCTION

In the past few years, interest in ion-selective electrodes as analytical devices has grown considerably. Their selectivity as well as their compactness and simplicity make these potentiometric devices attractive for laboratory or field use either as in situ probes or as components of chemical analysis systems for continuous or discrete water quality monitoring. By eliminating the need for discrete sampling, these sensors can provide an ideal method for obtaining truly representative measurements of the chemical parameters in the water environment. For in situ measurements, the environment itself becomes the sample, eliminating not only the contamination from sampling and holding containers, but also the time lag between sampling and analysis, during which time various chemical and biological alterations take place.

Presently ion-selective electrodes are available for many chemical parameters, and several are in use for marine chemical research, effluent and pollution monitoring, mixing studies, and baseline surveys. Despite these recent applications, very little work has been done on the performance and characteristic behavior of these sensors in a medium other than pure water, i.e., seawater. The accuracy, precision, reliability, and temperature dependence must be known before they can be used for meaningful measurements.

The Orion Divalent Cation Specific Ion Electrode can be used to measure the magnesium content in seawater or freshwater without sample pretreatment, and therefore lends itself to in situ applications. The concentration of magnesium is of interest in seawater, because it is a major constituent and is involved in sedimentation (dolomite) and sound absorption processes (as magnesium sulfate). In this study the Orion Divalent Cation Electrode #93-52 was evaluated for measuring the magnesium content in freshwater and seawater solutions at 10°C and 25°C.

SECTION 2

CONCLUSIONS

1. The modules which were supplied with the electrode were unstable and short-lived (~1 mo) despite the fact that both were used before the "expiration date." The replacement modules, however, performed well and lasted 3 months. Since the sensors have a short shelf life, they were on general back order and took over 3 months to obtain.

2. The height of the filling solution had no effect on the readings as long as it was above the sample solution.

3. The sensor response was a linear function of the logarithm of the concentration in fresh- and saltwater, with slopes in freshwater within 4% of the Nernst theoretical value.

4. The temperature drop to 10°C stabilized the electrode considerably, suggesting that the sensor should be subjected to low temperatures while soaking as a "break-in" procedure.

5. The sensor response in freshwater was quite slow (average 25 min), while in seawater the response was much faster (average 3 min). Since the drift was also much less in the seawater samples, the results indicate that the addition of an innocuous salt as an ionic strength adjuster (ISA) might be advantageous for freshwater samples.

6. Although two modules from Orion may have similar basic characteristics (i.e., response curves, temperature dependence, etc.), the electrode potential for two separate modules can be significantly different in the same solution with the same reference electrode.

7. Since the entire electrode body is made of hard plastic, the sensor was physically durable.

8. Although the calibration curves were fairly linear, the residual standard error (RSE) factor indicates that at least a three-point calibration is required to obtain reliable electrode slopes.

9. The sensor may be used for monitoring applications if (a) a daily calibration is possible (by automated standard addition if necessary), (b) the slow response time is not prohibitive, and (c) the samples are measured at the same temperature. When a standard addition method of calibration is not possible the electrode may be calibrated in solutions with the same background matrix as the samples, if the general composition of the sample is known, as in the case of seawater. The sensor is not affected by variations in light intensity or flow, and accuracies of 5% can be achieved when the modules are calibrated properly.

SECTION 3

EXPERIMENTAL PROCEDURE

INSTRUMENT DESCRIPTION

The Orion Divalent Cation Electrode Model 93-52 evaluated in this study was manufactured by Orion Research, Inc., to replace the older Orion #92-32 electrode. The specifications are given in Table 1. An external reference electrode is required in conjunction with the Orion Sensor to measure calcium, magnesium, or water hardness (calcium plus magnesium) in aqueous solutions. The reference electrode used in this study was the Orion Model 90-01 Single Junction Reference Electrode with the Orion #90-00-11 filling solution recommended by the manufacturer. The reference electrode was the "sleeve" type and is described by Ward (1978). The cation electrode is described in further detail in the Appendix.

Table 1. MANUFACTURER'S SPECIFICATIONS

Concentration range	6×10^{-6} to 1M
pH range	5.5 to 11 pH
Temperature range	0° to 50°C
Electrode resistance	2 to 8 megohms
Reproducibility	$\pm$ 4%
Sample	aqueous solutions only
Minimum sample size	3 ml in a 50-ml beaker, 0.3 ml in Orion Microsample Dish (Cat. No. 92-00-14)
Storage	store in air
Module life	6 months under normal laboratory conditions
Size	electrode length: 13.5 cm cable length: 75 cm cap diameter: 1.2 cm

The electrode potential was measured with an Orion Model 801A Digital pH/mV Meter with a range of ± 1999.9 millivolts (mV) in 0.1 mV increments and with ± 0.1 mV repeatability. The meter features high input impedance, extremely low drift, and an output displayed directly in mV. The meter drift was less than 0.2 mV over a 6-month period.

The electrode was secured in the top of a polypropylene container that was sealed to eliminate errors due to sample evaporation while submerged in a well-insulated, non-metallic constant temperature bath. The bath was constructed to maintain temperature to ± 0.01°C and to eliminate possible ground loops or stray electrical interferences, which frequently plague electrode measurements. The sensor was submersed at a constant 4 cm in the sample solution, which was stirred with a Teflon star-head magnetic stirring bar and a Troemner variable submersible stirrer. The temperature was monitored constantly with a Hewlett-Packard quartz crystal thermometer that was periodically calibrated against a platinum resistance thermometer. The sample solutions were suspended in the temperature bath prior to each run to remove possible changes in electrode potential due to temperature equilibration.

The salinities of the seawater samples were measured with a Guildline Model 8400 Laboratory Salinometer (Autosal) which has been described in detail by Boyd (1976). The natural seawater samples were analyzed for magnesium and calcium on a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer. The calibration curves and fits were determined by a least-squares method on a Hewlett-Packard 9825A Programmable Calculator.

The freshwater standard solutions were prepared from Fisher Certified ACS Reagent Grade magnesium chloride and Fisher Certified Atomic Absorption Standard Magnesium Reference Solution. The synthetic seawater solutions were also prepared from Fisher Certified ACS Reagent Grade chemicals using the formula of Kester (1967). The synthetic seawater solutions at 20- and 5-ppt salinities were prepared by weight-diluting the artificial 35-ppt seawater with pure water. The natural seawater samples were: (1) IAPSO Standard Seawater [P_{66} 27/7, 1974 - Cl (ppt) = 19.3675] at 35-ppt salinity, as well as at 20- and 5-ppt salinity by dilution with pure water; (2) Atlantic Ocean water (32.2-ppt salinity from a station at 38°40.3'N, 74°20.0'W) at 32- and 20-ppt salinity (diluted with pure water); and (3) Chesapeake Bay water at 4.2-ppt salinity. All dilutions were made with Millipore ion-exchanged (18 megohm) water.

TEST PROCEDURE AND RATIONALE

The electrode was evaluated with three different modules (see Fig. 1) at 10°C and 25°C in five different water types: pure water, synthetic seawater, IAPSO Standard Seawater, Atlantic Ocean water, and Chesapeake Bay water. The pure water tests were performed to observe the basic electrode characteristics without chemical interferences and only slight ionic strength effects. The sensor was calibrated with synthetic seawater to determine the electrode performance in a complex solution of known composition that simulated natural seawater and its matrix effects. The

subsequent electrode measurements in 35-, 20-, and 5-ppt salinity IAPSO Standard Seawater were made to determine the electrode accuracy after proper calibration with synthetic seawater and to observe the effect of salinity variations on the electrode response without relative compositional changes. Measurements were made in clean Atlantic Ocean water to determine variations in electrode response between IAPSO Standard Seawater (treated Atlantic Ocean water) and natural Atlantic Ocean water (untreated). Finally, the Chesapeake Bay water provided samples with an estuarine matrix and possible pollutant interferences.

The calibration curves in freshwater were obtained by measuring the magnesium (Mg^{2+}) activity in standard solutions ranging from 0.05 M to $1x10^{-3}$ M-Mg^{2+}. Two consecutive runs were made at 25°C -- the first in decreasing concentration step-changes, the second in increasing concentration steps. With this procedure the effects of directional concentration steps could be determined for response times, electrode calibration, and reproducibility (short-term drift). The electrodes were subsequently calibrated at 10°C and then again at 25°C in the same standard solutions as the other 25°C runs. From these tests, the effects of positive or negative temperature variations could be measured for response times, calibration curves, electrode slope, long-term drift (between the two runs), and durability to temperature changes. In each calibration run, the sensor was tested for: (1) short-term drift (3 hours); (2) sensitivity to flow variations; (3) sensitivity to different ambient light intensities; (4) response changes due to motion of the electrode and wire connections; (5) variation in electrode potential due to different filling-solution heights (reference electrode); and (6) electrode response as a function of time.

The calibrations in synthetic seawater were completed by measuring the magnesium activity in four standard seawater solutions with known amounts of magnesium and calcium (the Ca^{2+} was held constant in all four solutions). Immediately after calibration, values for magnesium activity were obtained in two different natural water samples at the same salinity as the standards. Since the relationship of magnesium activity to concentration is not known accurately in seawater (see Appendix) the results and calibration curves were calculated in concentration units. This procedure was completed at 35-, 20-, and 5-ppt salinity. The concentrations of the magnesium and calcium were determined from salinity measurements and atomic absorption spectrophotometry. From the seawater runs, we ascertained the effect of salinity on the electrode potential and response times, the stability and accuracy in various water types, sensitivity to variations in light intensity and organic content, and suitability for possible in situ monitoring in freshwater, estuarine, and seawater environments.

SECTION 4

RESULTS

CALIBRATIONS

Four evaluations were performed with three separate modules. The first sensor module, which came with the electrode, had large errors due to serious drift problems and a sensitivity to flow around the sensor. The performance steadily declined for 1 month after initial use, at which time the sensor module was deemed useless. The second sensor module (also provided with the electrode) was then assembled onto the electrode, and the tests were resumed (Evaluation #1). There were still some drift problems, and the sensor barely finished the tests before failing. At this time a new replacement sensor module was ordered and finally received more than 3 months later. Evaluations #2 and #3 were completed on this module. All sensors were used well before the expiration date stamped on the module container.

Seven calibration runs were performed in each evaluation - four in freshwater at 10°C and 25°C, and three in seawater at 35-, 20-, and 5-ppt salinity. The sensors were assembled and soaked in 0.1 M $MgCl_2$ for 2 days prior to the tests. All concentrations are given in molarity (M), defined here as the moles of magnesium (Mg^{2+}) per liter of solution.

The potential developed across the membrane was remarkably different between each of the three sensors in the same magnesium solution. At 25°C for example, in a 0.01 M solution, the three sensors recorded potentials of 65.2, -45.5, and 29.8 mV, respectively, against the same reference electrode. Obviously, the absolute value of the potential in mV is very dependent upon the individual characteristics of each module and can only be determined empirically by calibration in standard solutions. The electrode response (in mV) was plotted as a function of the logarithm of the magnesium concentration (M) and fitted to the equation

$$E = E^\circ + S \log M \qquad (1)$$

where E° is the intercept, S is the slope, and E is the electrode potential in a solution with M concentration of magnesium. The theoretical value for S for the divalent Mg^{2+} ion should be 29.6 mV/decade at 25°C. (See Appendix.) The values for E°, S, and the residual standard error (RSE) for the curve fits are given in Table 2 for the freshwater and seawater runs in Evaluations #1 and #2.

The calibration curves for the Orion electrode in freshwater are shown in Figs. 2-4. Evaluation #1 (Fig. 2) included calibration runs with the sensor modules supplied with the electrode. Although the sensor did not work well before the 10°C run, the results from Run #3, completed immediately after the low temperature run, were relatively good with an electrode slope of 33.8 mV/decade at 25°C. Freshwater Run #4 was performed after the seawater runs and shows that the module was obviously not responding properly at that time.

In Evaluation #2, the new replacement module performed well after the initial calibration was completed. (See Fig. 3.) Runs 2, 3, and 4 had very similar slopes of 28.9, 29.6, and 28.5 mV, respectively, and were quite close to the theoretical value of 29.6 mV decade. Similar to the first evaluation, the 10°C-calibration seems to have stabilized the sensor since Run #3 and Run #4 were very similar (Fig. 3). Although the electrode response was linear for all the runs in Evaluation #2, the slope did change somewhat with time, and the Mg^{2+} sensor would therefore require at least a three-point calibration to obtain reliable data.

The effect of temperature on the electrode response is shown in Fig. 4 for Evaluation #2. It is apparent that the sensor is temperature-sensitive and should be calibrated at the same temperature as the sample. For monitoring purposes, this problem could be eliminated by pulling the sample through a coil in a temperature exchanger to keep the samples at a constant temperature when in contact with the sensor head.

The seawater calibrations are shown in Fig. 5 as a function of salinity and magnesium concentration at 25°C. Although the electrode response was a linear function of the magnesium concentration (RSE $\leq$ 0.3), the slope decreased significantly with increasing salinity, the greatest effect occurring at a salinity near 35 ppt.

In general, the sensor worked well in all solutions, fresh-and salt-water, but required careful calibration with standard solutions with a background matrix and temperature very similar to that of the samples. As long as these factors are considered. the sensor is suitable for oceanographic application. The modules did not last as long as expected, however, and the sensors supplied with the electrodes did not perform well.

ACCURACY

The accuracy of the sensor was determined in natural seawater at 35-, 20-, and 5-ppt salinity by comparing the values for magnesium concentrations determined from the Orion electrode to the values obtained by analysis with the atomic absorption spectrophotometer. The electrode measurement of the unknown Mg^{2+} concentration in the natural water samples was completed immediately after the sensor was calibrated with four standard synthetic seawater solutions with a known Mg^{2+} content at the same salinity as the sample. The results are given in Table 3 as the percent error in the magnesium concentration determined with the electrode, compared to the "true" values determined with the standard laboratory methods. The results with the electrode were surprisingly good with an accuracy better that 5% in all the natural waters from 35- to 5-ppt salinity.

Table 2. COEFFICIENT FOR THE CALIBRATION CURVES

Water type	E° (mV)	S (mV/decade)	RSE
		Evaluation #1	
Freshwater			
25°C #1	93.4	21.63	10.3
#2	88.1	18.65	4.4
#3	71.1	33.82	2.2
#4	-43.4	- 1.43	7.3
10°C #1	78.3	37.67	2.4
Seawater			
5 ppt	-64.4	- 7.95	1.3
20 ppt	-44.8	12.32	1.7
35 ppt	-54.3	14.85	0.8
		Evaluation #2	
Freshwater			
25°C #1	114.1	41.81	2.0
#2	70.6	28.88	2.6
#3	135.5	29.65	3.1
#4	131.5	28.45	1.3
10°C #1	118.9	44.32	1.0
Seawater			
5 ppt	50.1	18.29	0.3
20 ppt	50.7	15.56	0.2
35 ppt	45.4	10.32	0.2

Table 3. ACCURACY[a] OF THE ORION DIVALENT ELECTRODE FOR MAGNESIUM MEASUREMENTS

Salinity (ppt)	Water type	% Error	% Precision[b]
35	IAPSO	4.2	1.6
	Atlantic Ocean	4.8	0.6
20	IAPSO	4.8	1.0
	Atlantic Ocean	0.2	2.6
5	IAPSO	4.1	4.4
	Chesapeake Bay	3.9	4.7

[a]The accuracy is given as the percent of the difference in concentration from the true value for Evaluation #2.

[b]The difference between two seawater runs at 25°C, divided by the true value.

RESPONSE TIME

The response times are given for Evaluation #2 in three different forms for this study: T_{95} (internal), T_{95} (external), and T_1 ($\pm$ 1mV). The first two are 95% responses (T_{95}), which are defined as the time required for the system output to attain 95% of the asymptotic value when subjected to a step input. The T_{95} is equal to three "time constants" ($1-e^{-1}$) of a pure exponential response.

The electrode potential was monitored continuously for 3 hours in each test solution, starting from the moment the sensor was immersed. The "internal" 95% response time, $T_{95}(I)$, is the time required for the electrode response to reach 95% of the change between the initial value and the final value in the same solution. The "external" 95% response, $T_{95}(E)$, is the time required for the sensor to each 95% of the change between the final potential in the current test solution and the final potential in the preceding test solution at a different concentration.

The $\pm$1 mV response time (T_1) is the time required for the electrode to reach within 1 mV (~7% in concentration units) of the final value. All three methods of expressing the time response gave similar trends (see Table 4) and were obtained by averaging all the tests in each individual run since the response was found to be independent of the concentration. The T_1 response time was considered to be the most useful parameter for discussing response time in this study, because it was recommended by the International Union of Pure and Applied Chemistry (IUPAC), and because it is less sensitive to the magnitude of the concentration step change than the other times if the concentration change is greater than 7%.

Table 4. RESPONSE TIMES[a] FOR THE ORION MAGNESIUM SENSOR

Water type		Time Response (min) $T_{95}(I)$	$T_{95}(E)$	T_1
Freshwater				
25°C	#1	35.3	14.0	12.0
	#2	56.8	56.5	42.4
	#3	32.3	14.5	19.0
	#4	46.0	48.5	29.7
10°C	#1	51.2	32.2	29.8
Seawater				
5 ppt	Synthetic	33.7	11.3	5.9 (0.3)[b]
	Natural	16.5	21.2	<0.1
20 ppt	Synthetic	19.3	8.9	3.0 (0.2)[b]
	Natural	3.3	10.8	0.1
35 ppt	Synthetic	17.2	13.8	1.2 (<0.1)
	Natural	35.5	36.8	<0.1

[a] Response times are reported in minutes.

[b] Values in parentheses are the time responses if soaked for 1 hour at the salinity of the sample.

In general, the electrode response was much faster in seawater than in freshwater, and even faster when the sensor was soaked in seawater at the salinity of the samples to be measured. (See Table 4, footnote b.) Surprisingly, the 10°C response times in freshwater were not significantly longer than those at 25°C. Runs #1 and #2 at 25°C were conducted in decreasing concentration steps, while Runs #3 and #4 were performed with increasing concentration steps. In these tests the response time was independent of concentration (down to 1×10^{-3}M) and unaffected by positive or negative step-changes in concentration.

The electrode responses have been plotted as a function of time in Figs. 6-11 for the Orion magnesium electrode as "Delta mV" versus time (in minutes) at 10°C and 25°C in freshwater and seawater. The "Delta mV" value is the change in the electrode potential at time (T) from the initial value obtained immediately after immersion in the test sample. In this manner, the electrode response at various concentrations can easily be depicted on one graph (bottle numbers correspond to various magnesium concentrations).

In freshwater, the first solution in which the sensor was immersed required an inordinate length of time to respond and stabilize. (See Figs. 6-8.) Even after 60 minutes in a solution, the sensor always exhibited some drift in most of the freshwater solutions. (See Table 5.) For purposes of calculating the response time, therefore, the electrode potential

was considered stable when the reading remained within ±0.2 mV over a 30-minute period. Despite the somewhat erratic behavior of the response times of the electrode in freshwater, the response time in seawater was much faster, possibly due to the high ionic strength. (See Figs. 9-11.) The unstable appearance of the sensor response in the seawater graphs (Figs. 9-11) is due to the necessity of expanding the mV axis to separate the curves for suitable viewing. As a result, a change of only 0.1 mV, which is not a significant variation, can be clearly seen on the curves.

DRIFT

The drift of the electrode potential is given in Table 5 for each calibration run and was monitored over five different time ranges. The short-term stability was calculated from the change in response over a 15-minute period after the sensor had "stabilized" (or had been immersed in the standard solution for 2 hours). The sample container was sealed to prevent concentration changes during the tests. The drift over a 1-day period was determined from the reading taken 3 hours after electrode immersion and the reading taken the following day in the same solution. The drift over 1 week was determined from the differences between the calibration runs completed 1 week apart in the same standard solutions. The drift over 1 month was calculated from the average difference between two calibration runs completed 1 month apart in the same standard solutions. The 50-day drift test was performed over a 50-day period during which the electrode response was continuously monitored in a sealed seawater sample at a constant temperature. The 2-hour, daily, weekly, and monthly drifts are summarized in Table 5. The 2-hour drift is expressed as the change in millivolts over a 15-minute period after the electrode was immersed in the sample for 2 hours, and was averaged over the entire calibration run.

From Table 5, it is apparent that the short-term stability improved considerably after the 10°C run was completed and the sensor was returned to 25°C (Runs 3 and 4). While the weekly and monthly drifts were quite large in freshwater, the sensor was stable to within ±3 mV in seawater (See Table 5 and Fig. 12) for at least 30 days. After 35 days, however, the sensor response deteriorated until the potential had decreased by 19 mV after 50 days (Fig. 12). The magnesium and calcium concentrations were measured before and after the test to ensure that the concentrations in the sample had not changed during the test. The drifts of the electrode in the natural water samples were found to be the same as that in the synthetic seawater.

Table 5. DRIFT OF THE ORION MAGNESIUM ELECTRODE

Time period	Water type			ΔmV[a]
2 hours[b]	Freshwater	-25°C	#1	0.5
			#2	1.8
			#3	0.1
			#4	0.1
	Freshwater	-10°C	#1	0.9
	Seawater	5 ppt		0.1
		20 ppt		0.1
		35 ppt		0.1
1 day[b]	Freshwater	-25°C		1.7
		-10°C		1.7
	Seawater[c]	-25°C		2.5
1 week	Freshwater	-25°C		11.0
1 month	Freshwater	-25°C		44.3
50 days	Seawater	-25°C		19.0

[a]Change of 0.2 mV corresponds to an error of 0.7% in concentration.

[b]Averaged over entire calibration run.

[c]Values for natural water were the same as those in synthetic seawater.

ENVIRONMENTAL EFFECTS

The Orion electrode was subjected to various light intensities to determine if light attenuation (or variations in "turbidity") could affect the electrode potential as some studies have reported (Bates,1973). The effect of variations in environmental conditions (light, flow, external motion) on the electrode were determined and are summarized in Table 6. In Evaluation #1, the electrode sensitivity to light increased over a short time from ±0.2 mV. After the tests were completed, the electrode was found to be defective. Similar problems were found in the flow and motion tests. Apparently the module became generally unstable as it began to fail. In Evaluations #2 and #3 the sensor was unaffected by light changes, flow variations around the electrode, or external motion of the connecting wires and electrode body.

Table 6. ENVIRONMENTAL EFFECTS[a] ON THE ORION SENSOR

Parameter	Eval. #1	Eval. #2	Eval. #3[b]
Light	± 0.2	0.0	0.0
Flow	± 0.3	±0.2	±0.1
External Motion	± 0.2	±0.1	±0.1

[a]Changes in mV due to parameter applied.

[b]Conducted only for environmental effects after Evaluation #2 had been completed.

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APPENDIX - INSTRUMENT THEORY

The Orion Divalent Cation Electrode #93-32 consists of an electrode body and a pre-tested sensing module, which is activated by screwing the module into the electrode body. The module should be good for 6 months and consists of an organophilic-porous membrane surrounded by a porous plastic reservoir saturated with liquid ion-exchanger (Fig. 1). The internal aqueous reference solution is located on the inside of the membrane and is also in contact with silver/silver chloride (Ag/AgCl) internal reference element.

A process of ion-exchange takes place at the membrane interface between ions of the "ion-site" salt in the organic phase and the free ions in the aqueous phase. The selectivity of the sensor depends primarily on the selectivity of this "ion-exchange" process. Once inside the liquid membrane, the site and ion move together through the membrane phase. Rejection of unwanted ion can be achieved by blocking either the ability of the ion to pass into the membrane solution or the movement of the ion in the membrane phase. The liquid phase also solves the problem of ensuring the mobility of the "sought for" ion since the ion will be free to move by diffusion. The internal solution contains a fixed activity of the ion to which the membrane is permeable. When the electrode is placed in a sample solution, there is a momentary flux of ions across the membrane system in the direction of the solution containing the lower activity of the mobile ion. Since each ion carries a charge, an electrical potential is set up that opposes further ion migration. Eventually, an equilibrium is established in which the potential across the membrane is exactly that required to prevent further net movement of ions.

The changes in membrane potential can be measured by making electrical contact to the internal aqueous solution with the internal reference element (Ag/AgCl). At the same time, the sample solution is contacted with a second external reference electrode via a salt bridge. A high input impedance voltmeter connected across the two electrode leads will indicate a potential given by the Nernst equation:

$$E = E^\circ + 2.3 \frac{RT}{zF} \log A \qquad (A1)$$

where E is the potential in millivolts (mV) developed by the system, A is the activity of the ion to which the membrane is permeable, and E° is a constant potential developed by that particular electrode system. The E° term depends on the type of reference electrode used, the ionic activity in the inner solution, and the small potential due to the liquid-liquid junctions at the salt bridge connections (reference electrode). The $2.3\ RT/zF$ term is called the "Nernst theoretical slope", where R is the universal gas constant, T is the temperature in °K, F is Faraday's constant, and z is the charge on the ion (+2 for magnesium or calcium). The Nernst slope at 25°C for a divalent ion is 29.6 mV per decade of activity (Durst, 1969). At this point, it is important to note that ion-selective electrodes respond to changes in ionic activity, not concentration.

The activity of an ion can be thought of as the "effective concentration" of the free ion in solution and is affected by temperature, pressure, ionic interactions (i.e., ion complexation or ion-pair formation), and ionic strength (a chemical parameter related to the number and charge of all the ions in the solution). The activity (A) is equal to the product of the ionic "activity coefficient" (γ_+) and the total concentration of the ion (m)

$$A = \gamma_+ m_+ \qquad (A2)$$

where γ_+ is a function of ionic strength (I) and ionic interactions. Even if the electrodes were truly "specific" and responded to the ion desired, the sensor response would be affected by only the free ionic activity, not the total concentration. Since many chemical species in natural waters are complexed with other ions or adsorbed on particulate matter, a large fraction of the element may not be detected by these sensors.

Ideally, the electrode pair would be calibrated with standard solutions of known activity, and the electrode potential would be fitted to the Nernst equation. In a plot of E (mV) versus the logarithm of the ionic activity, the slope should be equal to the Nernst slope (2.3 RT/zF) and the intercept equal to E°. The basic problem with this "ideal" situation is that the activity coefficient can only be determined for salts and not for a single ionic species. For example, although the $\gamma_\pm$ for potassium chloride (KCl) is known in pure water, the γ_+ for K^+ can only be estimated by somehow splitting the $\gamma_\pm$ (KCl) into its ionic components with some arbitrary convention. One of the most common methods in use today is the McInnes Convention, in which it is assumed that $\gamma_+ (K+) = \gamma - (Cl^-)$. Since this is only an arbitrary convention, it is obvious that the γ_+ for an ionic species cannot be accurately determined, even in pure water.

In natural waters, the situation is much worse due to the presence of many other ions in the solution, all of which affect the value of γ_+ to a certain extent. To circumvent this problem, a "working curve" can be established for sensors in natural waters in which the electrode potential is determined as a function of the logarithm of the concentration of the desired ion. In this case, the value of γ_+ (ion) is not known and, therefore, the electrode must be calibrated in solutions which not only contain known concentrations of the desired ion, but also duplicate the background "matrix effects" of the other ions in the sample. Since the activity of the ion is the same in both the standards and the sample, a reliable calibration can be prepared in terms of total concentration. An electrode measurement in seawater, therefore, requires the calibration of the sensors in standard seawater solutions with a known concentration of the desired ion and a background matrix which simulates the composition of the sample as closely as possible.

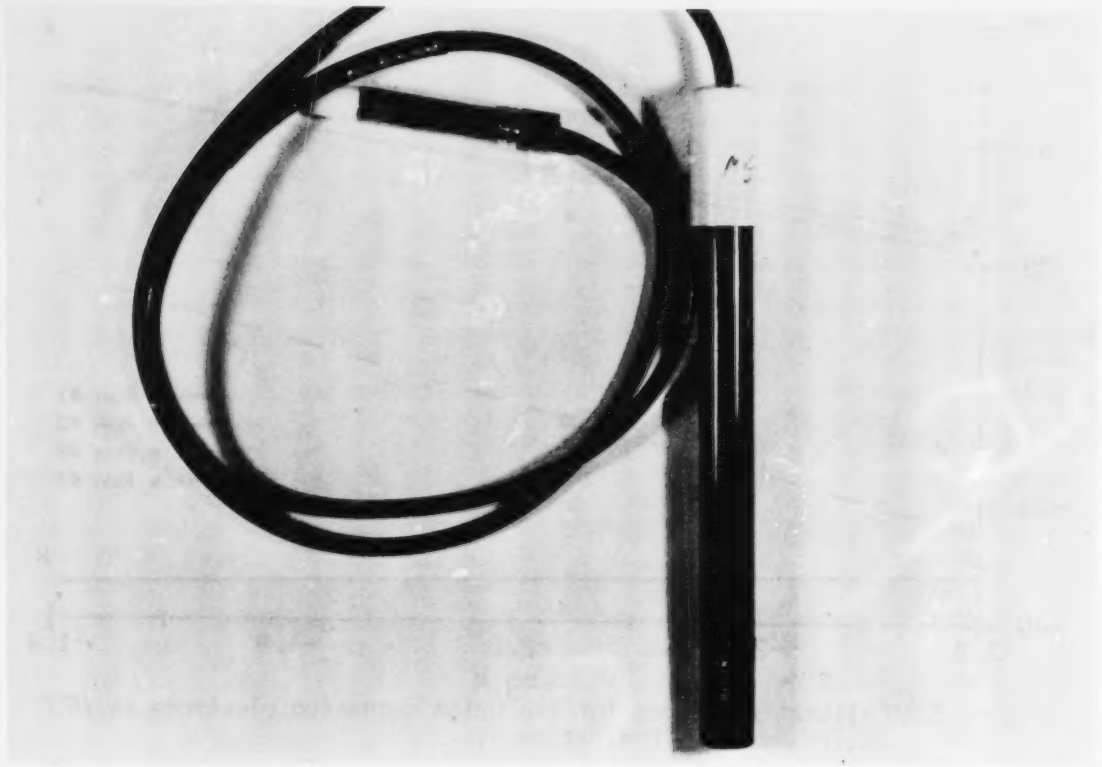

Figure 1. Sensor module for the Orion #93-32 Divalent Cation Electrode.

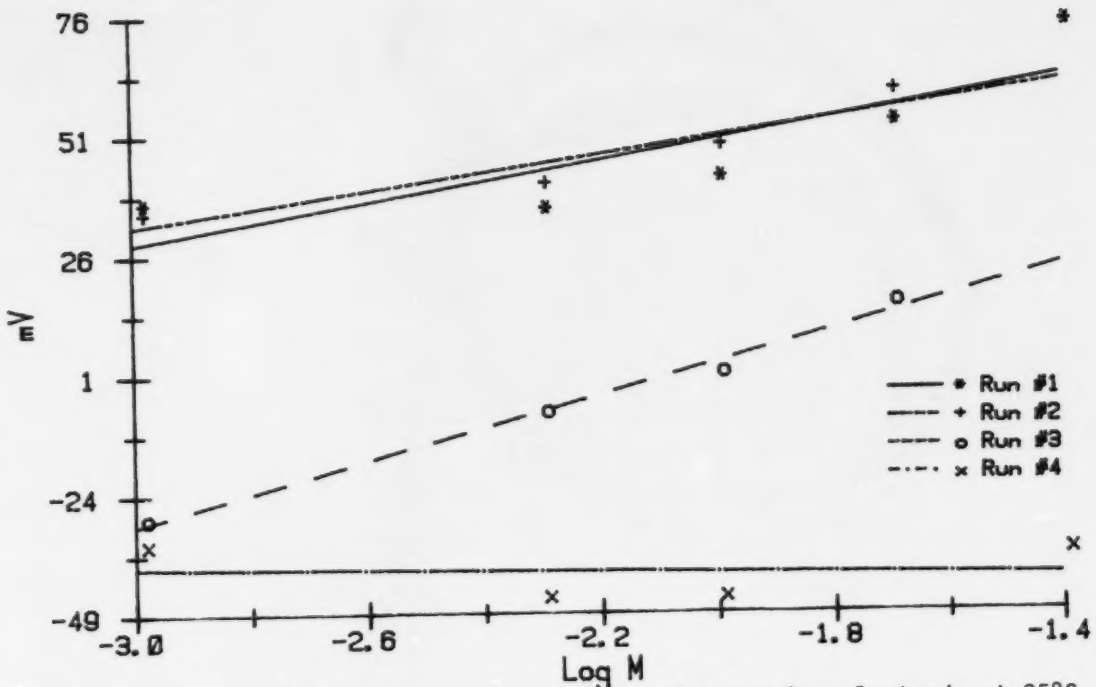

Figure 2. Calibration curves for the Orion magnesium electrode at 25°C in freshwater - Evaluation #1.

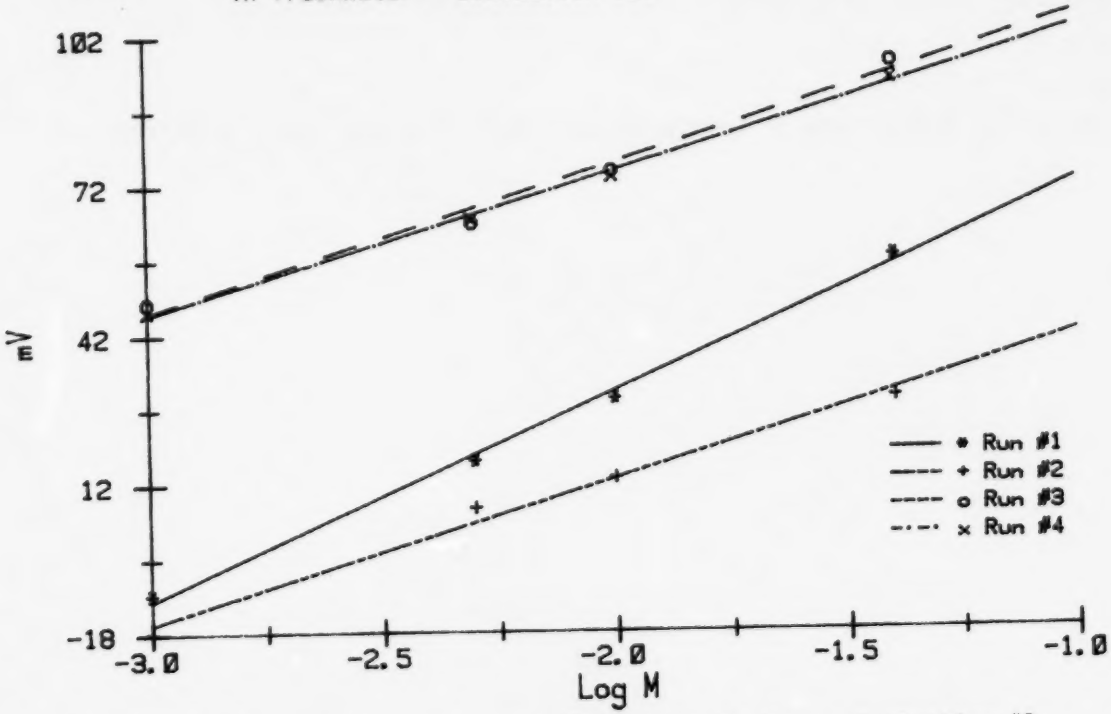

Figure 3. Calibration curves at 25°C in freshwater - Evaluation #2.

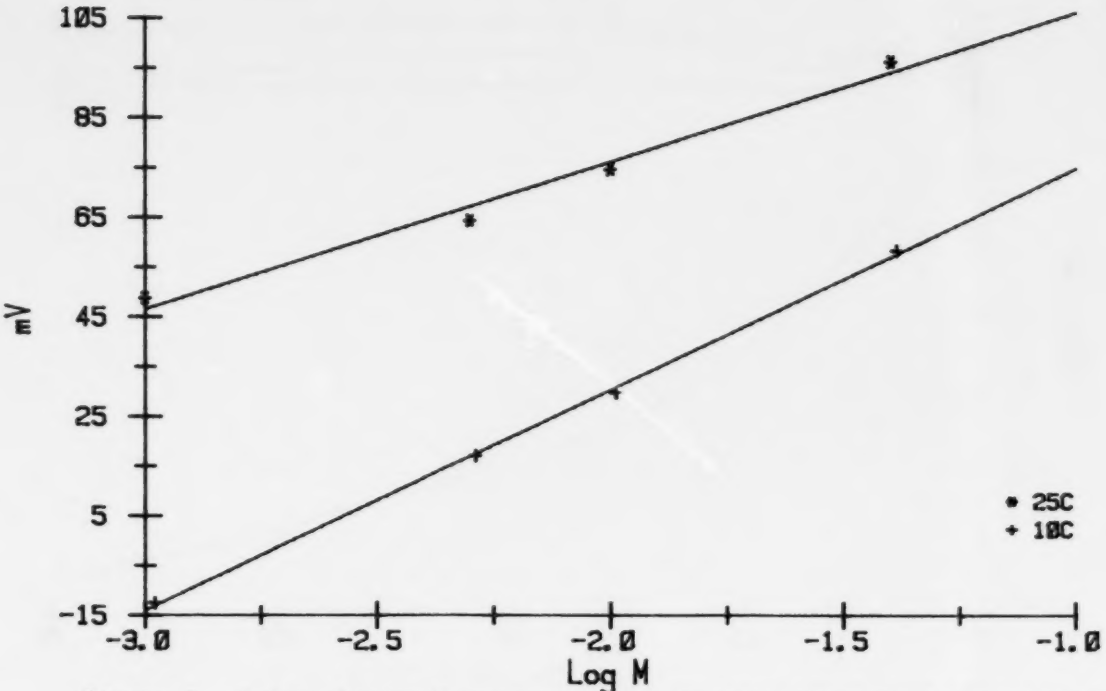

Figure 4. Orion electrode response as a function of magnesium concentration and temperature in freshwater.

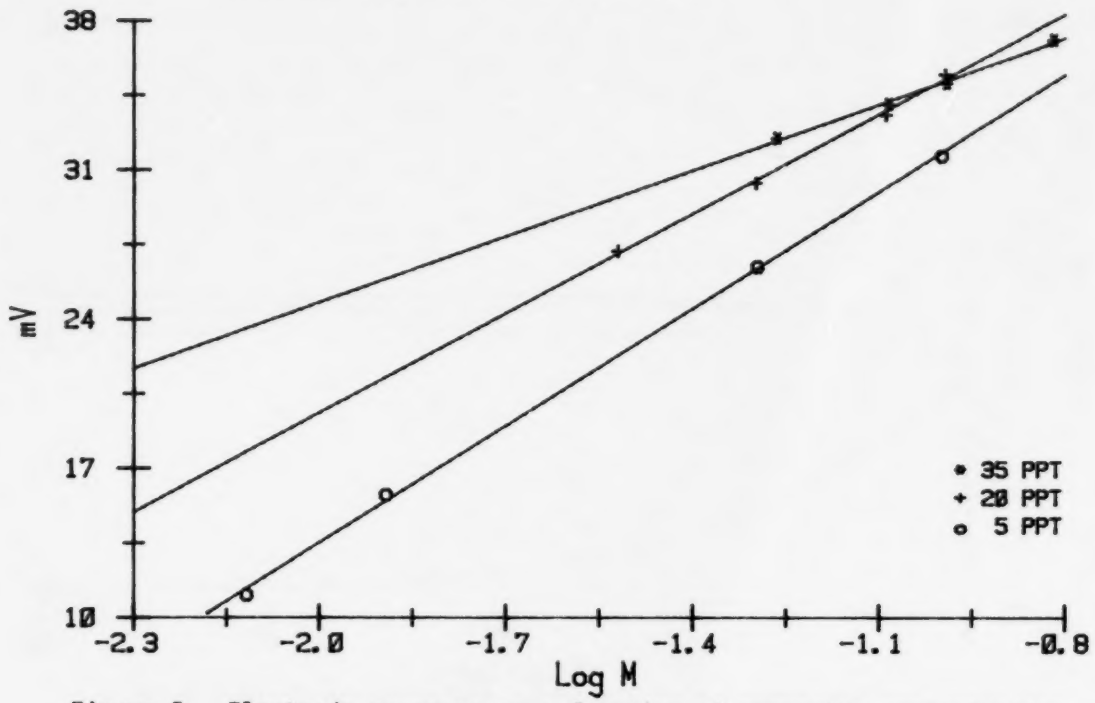

Figure 5. Electrode response as a function of magnesium concentration in 35-, 20-, and 5-ppt salinity seawater at 25°C.

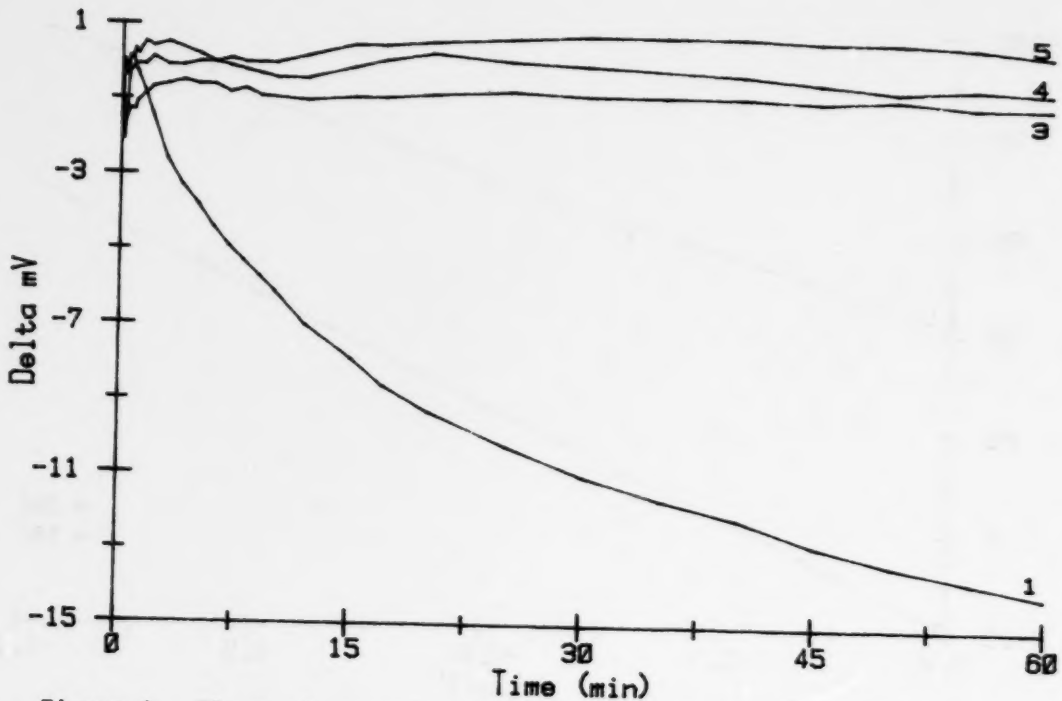

Figure 6. Electrode response at a function of time (min) and concentration in freshwater at 25°C - Run #1.

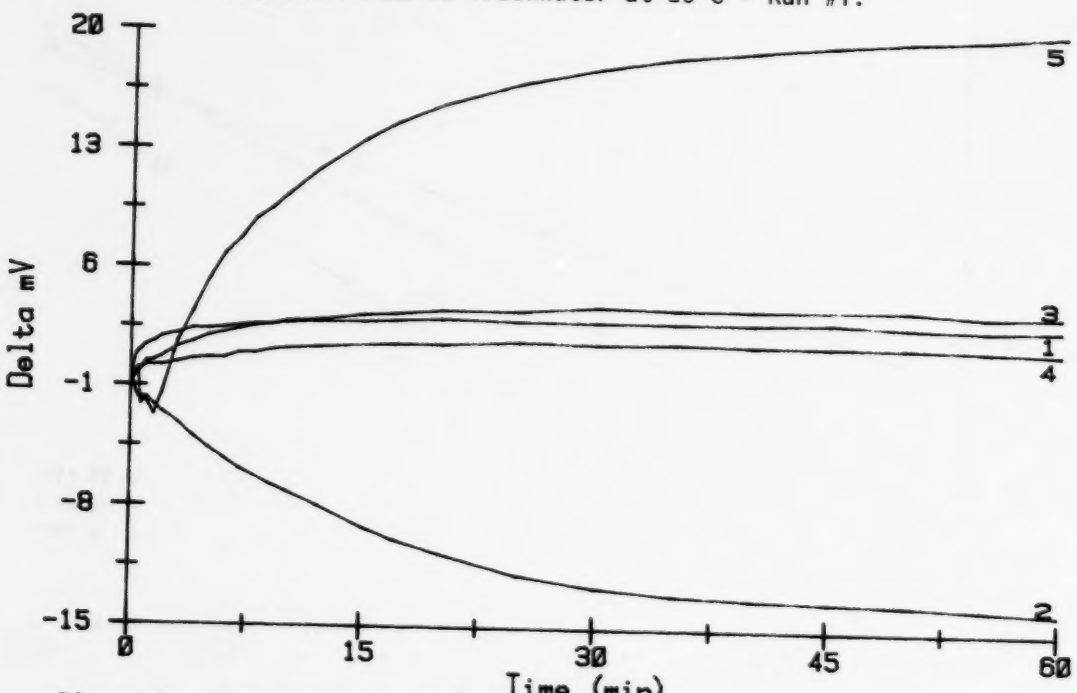

Figure 7. Time response of the Orion electrode in freshwater as a function of magnesium concentration at 25°C - Run #3.

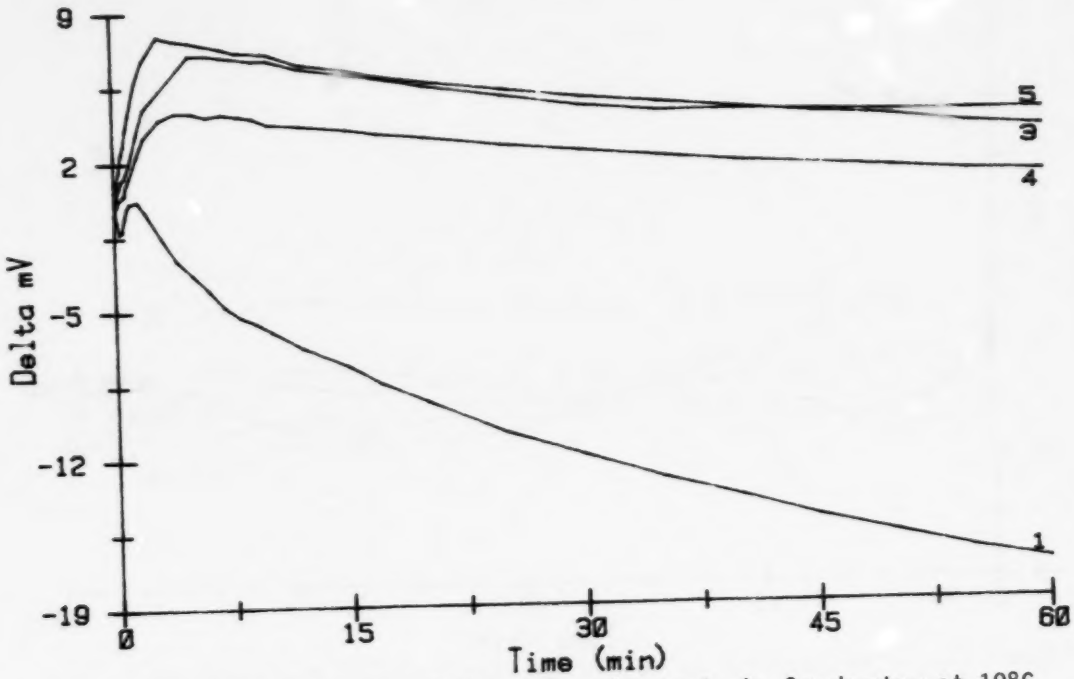

Figure 8. Time response of the Orion electrode in freshwater at 10°C.

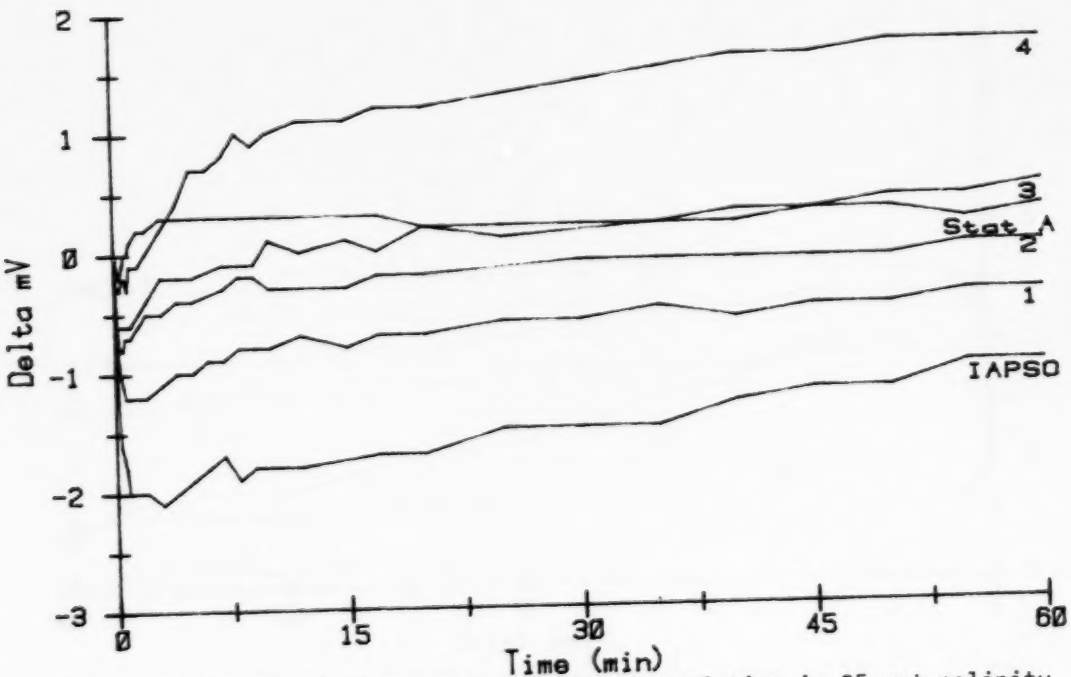

Figure 9. Electrode response as a function of time in 35-ppt salinity natural and synthetic seawater at 25°C.

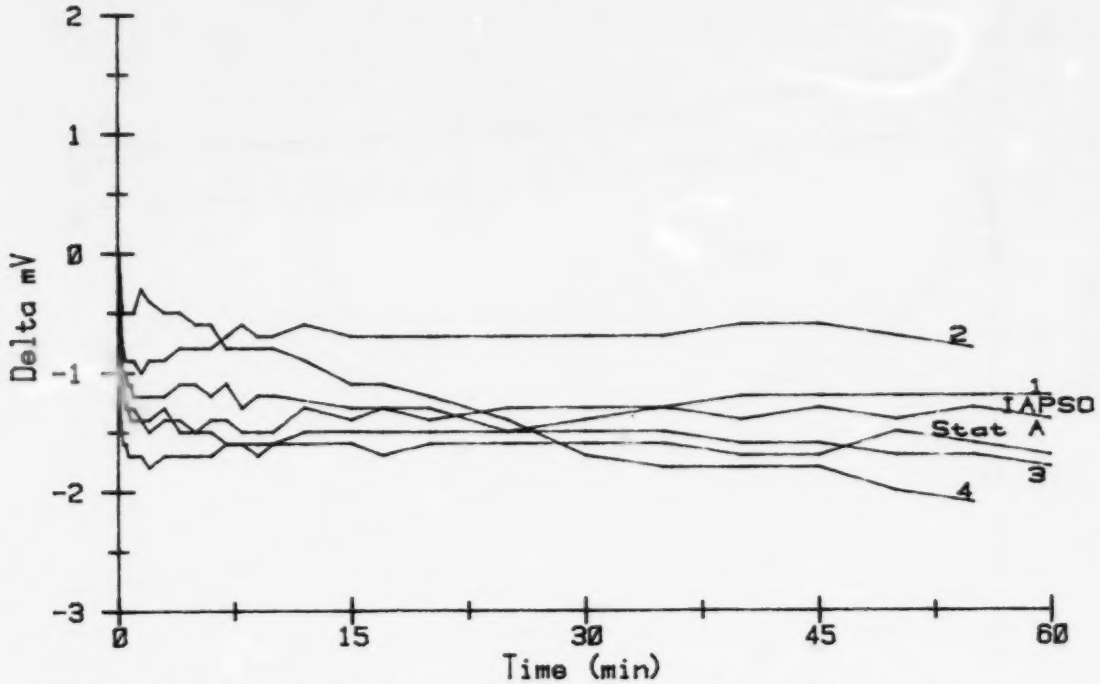

Figure 10. Time response of the Orion electrode in 20-ppt salinity seawater.

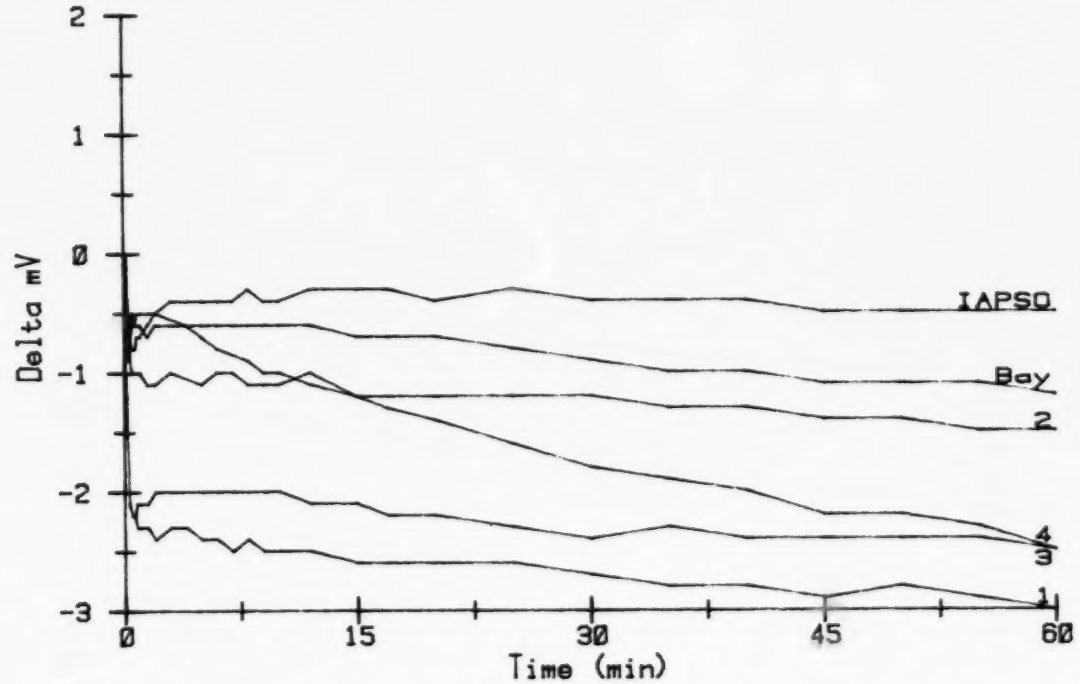

Figure 11. Time response of the Orion electrode in 5-ppt salinity seawater.

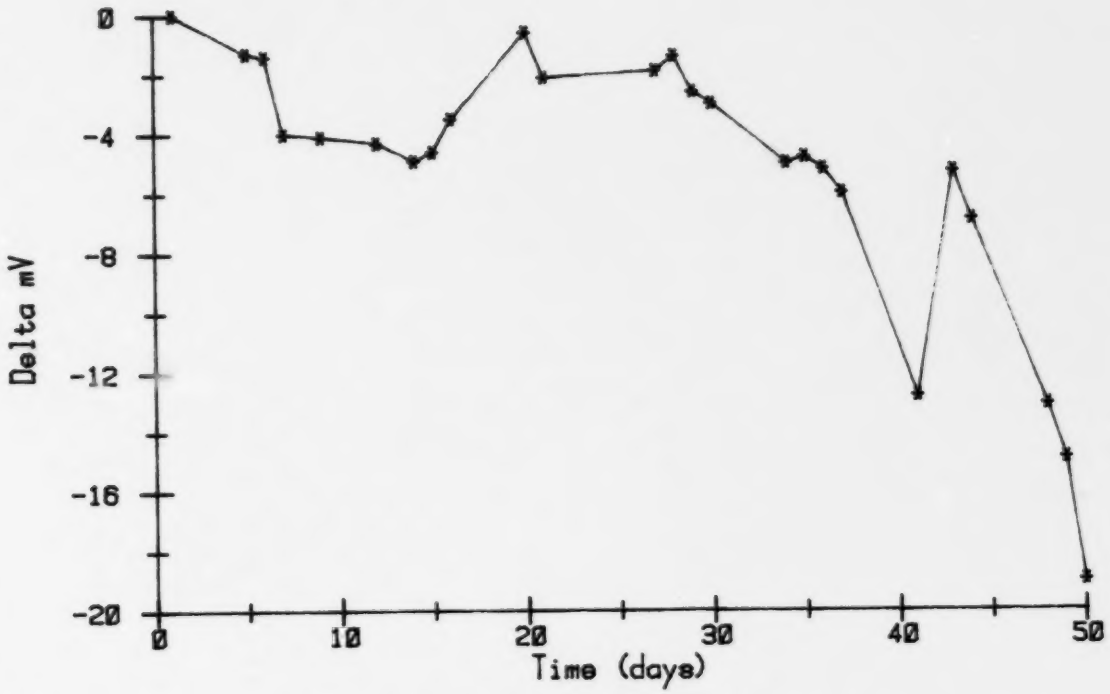

Figure 12. Drift in electrode potential at 25°C over a 50-day period at constant magnesium concentration in seawater.